

# A COMPARISON OF GRAPHITE OXIDATION KINETICS

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## Introduction

Graphite is used in a wide variety of applications, ranging from electrodes to nuclear moderators and, due to its excellent thermal conductivity, even in break linings for heavy vehicles like aircraft. During these high temperature applications the oxidative behavior of the graphite is important and in the case of nuclear reactors this is especially true during emergency situations where the graphite could be exposed to air at very high temperatures (> 800°C) with potentially harmful implications. The purpose of this study is to compare the relative reactivities of graphite samples from natural (NG) and synthetic (SG) origins.

## Experimental

Four proprietary graphite samples with unknown pre-processing were chosen due to availability, two from natural origins and two which are synthetically produced. The samples were characterized using isothermal TGA (Thermogravimetric Analysis). The tests were conducted on a TA Instruments SDT Q600 under atmospheric pressure. Powdered samples (ca. 1 mg) were placed on open 90 µl platinum pans. During the isothermal runs the samples were heated at a scan rate of 10°C/min in instrument grade argon flowing at 300 ml/min from 25 °C to temperatures between 600 and 800 °C. When the desired reaction temperature was achieved the nitrogen flow was shut off and oxygen flow was started at 300 ml/min. The experiment was repeated three times for each graphite at different temperatures. The dynamics of the gas change from inert to reactive were found to be negligibly quick using mass spectrometer (QMS600) connected to the furnace outlet.

The X-ray Diffraction (XRD) spectra of the samples were obtained using a PANalytical X-pert Pro powder diffractometer with variable divergence and receiving slits and an X'celerator detector using Fe filtered CoKα radiation. In addition, Scanning Electron Microscope images were obtained on an ultrahigh resolution field emission SEM (JEOL 6000F). The presence of impurities was checked using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

## Results

The solid state kinetic approach was used to model the observed behavior. This approach is widely applied to gas-solid reactions and is based on a differential equation derived from homogeneous chemical kinetics [1, 2]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) P_o^r \quad (1)$$

Here  $\alpha$  is the dimensionless degree of conversion and  $f(\alpha)$  is the reaction model or conversion function applicable to the situation at hand [3, 4]. It describes the influence of sample morphology and characteristics on the burn-off rate.  $P_o$  is the partial pressure of the reacting gas, in this case oxygen, and  $r$  is the gas-phase reaction order. The gas was assumed to behave ideally and a simple Arrhenius expression was assumed for the temperature dependence of the reaction rate constant,  $k(T)$ . This allowed equation (1) to be modified as follows:

$$\frac{d\alpha}{dt} = k_0 P^r \exp\left(-\frac{E_A}{RT}\right) f(\alpha) y_o^r \quad (2)$$

Where  $y_o$  is the oxygen mole fraction and  $P$  is the system pressure, which are both equal to 1 given that the runs were done in pure oxygen at 1 atmosphere. To illustrate the similarity of the sample temperature dependence, the same value for the activation energy ( $E_A$ ) was used for all samples. Based on work done on HOPG [5] a value of 175 kJ/mol was chosen. Finally pre-exponential factor ( $k_0$ ) can be arbitrarily chosen to scale the curves such that  $0 < f(\alpha) < 1$ , which allows easy comparison. The values for  $k_0$  are shown in Table 1. These scaled curves now represent the conversion function of a particular sample and these are shown in Figures 1 to 4. It should be noted that natural graphite type B has been compensated to exclude the ash content.

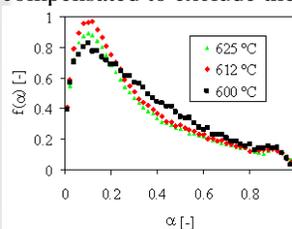


Fig. 1 Conversion function NG1

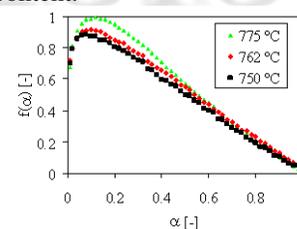


Fig. 2 Conversion function NG2

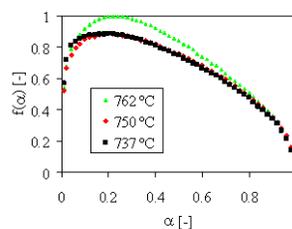


Fig. 3 Conversion function SG1

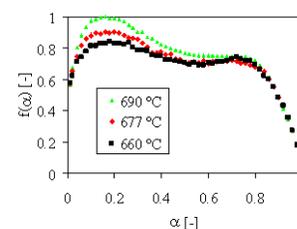


Fig. 4 Conversion function SG2

Table 1. Pre-exponential factors.

	NG1	NG2	SG1	SG2
Pre-Exponential factor ( $k_0 / 1e6$ ) [min.atm] <sup>-1</sup>	280	20	16.7	61

## Discussion and Conclusions

As can be seen from Figures 1 to 4 the conversion functions differ widely for the four graphite samples under consideration. Despite the fairly arbitrary assignment of the activation energy the conversion functions show good unification if one considers the fact that for each 12 °C increment in reaction temperature the reaction rate increases by 30%, given an activation energy of 175 kJ/mol.

Furthermore this approach allows a very straightforward comparison of the relative reactivities of the samples via the pre-exponential factors given in Table 1. It is notable that none of the samples conform perfectly to the theoretically expected behavior for graphite flakes with an inert basal plane, i.e. a shrinking disc reacting only from the edges.

A variety of factors are responsible for the deviations from the ideal behavior. These can be widely classified into the following categories: crystal domain size, catalytic activity, particle size distribution and particle microstructure.

The effects of crystal domain sizes are very evident when comparing the effect of oxidation on the synthetic material to the natural. As can be seen from Figure 5 the basal plane of the oxidized synthetic material is heavily irregular compared to that of an oxidized natural sample, shown in Figure 6. This finding is further substantiated by the XRD traces which allow the calculation of the crystal domain sizes from the half-peak width of the 002 peak ( $2\theta = 30.8^\circ$ ) [6]. The domain sizes have been calculated as 597 and 532 nm, for the type A and B natural graphite and as 257 and 307 nm, for the type A and B synthetic graphite respectively.

Catalytic activity is most noticeable in the natural materials as can be seen from the highly erratic, almost fractal like edge roughening (Figure 6). The ICP-MS analysis confirmed the presence of known metallic catalysts including iron and potassium [7, 8] in the natural samples, but the synthetic materials on the other hand have a very low impurity content. It is also interesting to note that the sample with the highest metallic impurity content, natural graphite type B, has the second lowest reactivity. Thus it is clear that impurity levels alone are not an unambiguous indicator of the effect of catalytic activity on graphite reactivity.

The particle sizes of the samples are very similar with the exception of natural graphite type B which is composed of significantly larger flakes than the other samples. This could explain the lower reactivity of this sample since one would expect a lower active surface area to volume ratio for larger flakes.

During visual inspection of the synthetic samples, distinct particle microstructures are discernable within a single sample. These are presumed to be due to the particles' origin, i.e. coke particles vs. residual pieces of the binder phase. The binder particles show extremely complex microstructures with highly variable amounts of active surface area and complex pore structures. This is very different from the simple flake like natural graphite particles (type B) and one would expect this to contribute significantly to the particles' reactivity. Type A natural graphite tends to form large agglomerates which may also behave as a single large particle with a complex pore structure. These pore structures lead to the possibility that internal mass transfer limitations are present during oxidation.

Whilst care was taken to avoid external mass transfer limitations by conducting control experiments at different purge rates, it is difficult to determine whether internal limitations are present without samples of varying particle size from the same source. Additionally, the possibility that

different types of surface complexes are evolved on the different graphite samples during oxidation, especially at different temperatures, should also be considered when coming to conclusions regarding the inherent reactivity of the graphite under consideration.

This paper illustrates the complexity when comparing fairly pure graphite samples from different origins with unknown pre-processing. It is difficult to easily distinguish between effects due to impurities and the intrinsic characteristics of the graphite, since multiple combinations of these factors affect most of the graphite samples in varying proportions. The need exists for a systematic approach to characterizing all the factors affecting graphite oxidation to allow sensible comparison of samples from different origins.

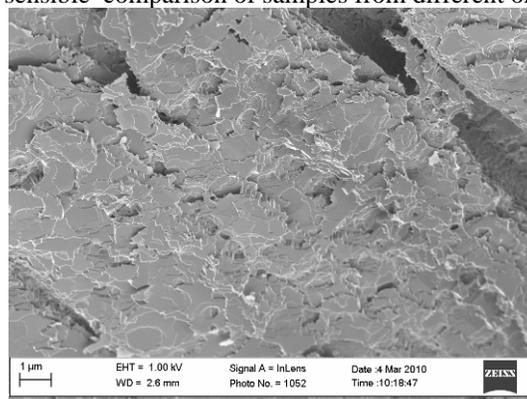


Fig. 5. Oxidized synthetic graphite type A.

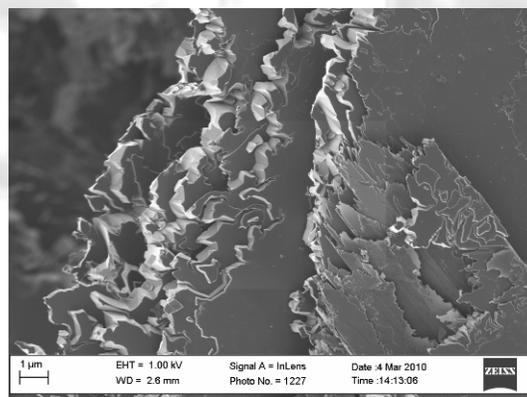


Fig. 6. Oxidized natural graphite type A.

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